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Energy Distribution in Luminescence Spectra of Organic Compounds

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by

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PROGRESS REPORT

Energy Distribution in Luminescence Spectra

of Organic Compounds

As stated in the Research and Development Task Order N6onr-23112:

"Contractor - - - shall conduct research on energy distribution in luminescence spectra of organic materials. Such research shall include, but not necessarily be limited to the following: studies of aniline, o-, m-, and p-diphenyl amine, carbazole, p-difluorodiphenyl, diphenyl, 4-nitro diphenyl, lycopene, fluorescein (acid), phenazine and eosine."

To this list we now wish to add anthracene, chlorophyll and chlorophyllin derivatives as well as various phthalocyanines.

In order to carry out this assignment it has been necessary to purchase or build the following equipment: a synchronous motor; a rotating disk with holes to chop the light from the luminescing solid, liquid or solution, in order to be able to amplify it; an Adam Hilger infrared constant deviation spectrometer; a lead sulfide infrared detector cell; a high gain amplifier to amplify the signal output of the lead sulfide cell; and various meters, lenses, lens mounts, small optical benches, etc.

Detail of Experimental and Developmental Work

1. A four foot, sturdy optical bench to carry part of the above equipment was designed and has been built.

2. After considering various possibilities we decided to build a high gain amplifier designed for infrared work in stellar physics by W. Wilson of Northwestern University and reported by Kuiper, G. P., Wilson, W., and Cashman, R. J., in the Astrophysical Journal 106, 243 (1947) under the

title "An Infrared Stellar Spectrometer". The amplifier was designed for use with the lead sulfide cell, and is to be used in the same way by us.

The Wilson Amplifier consists of a pre-amplifier and a main amplifier with a total voltage gain of 3×10^7 or about 150 decibels. The amplifier is tuned to 1080 c.p.s. and is supposed to permit transmission of a band as narrow as 1 c.p.s. Because of the unusually high gain of the amplifier, the noise constituted quite a problem. An unusually large amount of time was required in efforts to shield and check every critical point. So far we have been able to reduce the noise generated in the amplifier to about 20% of the noise generated in the photo-cell. Most of the remaining noise comes from the tubes of the first stage amplifier. The photo-cell noise produces an input voltage of a few micro-volts. In the course of various adjustments, it was found advantageous to isolate the power supply from both the pre- and the main-amplifier and to use a storage battery for the heaters.

To further improve the signal/noise ratio as recorded by the output meter an RC-filter was used to reduce output noise components in the neighborhood of zero frequency. In this connection, see Nelson and Wilson, Proceedings of the National Electronics Conference, Chicago, Nov. 1947, page 584. It is our hope that by the above modifications an improvement of the signal/noise ratio can be achieved, increasing it by a factor of about five.

3. A synchronous motor of 1800 RPM was borrowed from the High Altitude Laboratory for preliminary tests, and was found to have sufficient power to drive the rotating disk at a constant speed. We then purchased one of the same type, RWC 2505, No. 233 LC, 9 watts, 0.15 oz. in. torque, from Holtzer-Cabot in Boston. By means of a mount, the motor was attached

to the optical bench.

4. A rotating aluminum disk having 36 holes to chop the light at a rate of approximately 1000 c.p.s. has been built. Round holes were used for ease of cutting. The diameter of the holes was chosen equal to the length of the entrance slit (1 cm.). The distance between the holes was chosen such that the area between two adjacent holes and their two common outer tangent lines equalled the area cut out by one of the holes. This arrangement appeared to give most nearly a sine-wave modulation of the light. A sine wave is desirable because, under these conditions, all the energy of the 1000 c.p.s. signal is transmitted by the amplifier. Otherwise much of the energy would be lost to harmonics not transmitted by the amplifier.

5. Two PbS-cells have been purchased. One of these is from Eastman Kodak Company and the other from Citron. Preliminary tests show no significant differences between the two. Inasmuch as different cells show maximum response at different wavelengths, we may find it advantageous to choose different cells for different spectral regions.

6. A six inch optical bench has been built to carry condenser lenses in front of the entrance slit. It permits accurate adjustment in all three directions of space. A similar bench is planned to condense the light from the exit slit on the photo cell.

7. A mount for the Kodak photo cell has been constructed, and is so designed as to be able to replace the eyepiece of the spectrometer. A mount for the Citron cell is also planned which will take the place of the thermocouple of the Hilger instrument.

Preliminary Tests

Preliminary runs with the above equipment show that we can easily detect about six lines in the mercury spectrum between 1 and 2 microns (10,000 to

20,000 Å). It is also possible to detect the infrared radiation in the same region emitted by a lighted cigarette placed about three yards from the entrance slit.

Possible Future Directions of Work

In our rather extensive literature search, it has become evident that we need to know more about the following subjects:

1. The physical properties of lead sulfide cells including nature of sensitive spots, temperature coefficient of sensitivity, etc.

2. Suitability of other methods of detecting infrared radiation, such as the transistor photo cells.

3. Best procedures to follow in infrared work such as the question of various light choppers (rotating disk with series of holes, Kerr-cell, etc.) Also the use of wobble methods including oscillating mirrors and gratings. Value or disadvantage of the use of elipsoidal mirrors frequently mentioned in the literature. According to W. E. Forsythe reporting in the Astrophysical Journal 45, 278 (1917) there is a so-called "best axis" about which the prism of a constant deviation spectrometer should rotate. It may be possible to improve our instrument by some adjustments of this type.

4. High gain amplifiers may possibly be improved so as to be able to study a narrow band and there may be ways of integration so as to build up the signal above the noise level. The question of the advantages of "gating" the amplifier needs to be studied.

5. It may be advantageous to obtain some frequency standard which is more accurate than the line frequency to drive the synchronous motor.

6. Since it is obvious from our literature search that very little has been published on luminescence in or near the infrared, it becomes necessary to know more about the nature of those compounds which do emit radiations in

the red or near infrared. Having this knowledge the task of discovering new radiators is simplified.

7. A question which frequently presents itself is that of the exact range of frequencies assignable to electronic shifts and the place in the spectrum where vibrational energy shifts of the atoms begin to show up. If these questions could be answered, we might also learn where rotational energy shifts become obvious. At present all knowledge of rotational and vibrational energy changes comes from a study of absorption and Raman spectra, but it seems reasonable that here too there must be an emission (even though we have not been able to observe it, if there is an absorption.